PATENT ABSTRACTS OF JAPAN

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(54) METHOD OF PRODUCTION FOR CARBON NANOFIBER

(57)Abstract:
PROBLEM TO BE SOLVED: To produce carbon nanofibers with well-developed graphite structure in an industrial scale.
SOLUTION: The method comprises bringing raw material gas including a carbon compound into contact with a catalyst substantially comprising a metal having maximum diameter ≥1 μm, at a high temperature.

CLAIMS

[Claim(s)]
[Claim 1]A manufacturing method of a carbon nano fiber of the shape of black lead contacting material gas containing carbon compounds for a catalyst to which an overall diameter changes from metal of 1 micrometers or more substantially, and making a carbon deposition reaction occur for it.
[Claim 2]A manufacturing method of a carbon nano fiber of the shape of black lead contacting material gas containing carbon monoxide for a catalyst which comprises metal particles with a particle diameter of 1 micrometers or more substantially, and making a carbon deposition reaction occur for it.
[Claim 3]A manufacturing method of the carbon nano fiber according to claim 1 or 2, wherein material gas contains hydrogen.
[Claim 4]A manufacturing method of the carbon nano fiber according to any one of claims 1 to 3, wherein a catalyst comprises metal of the 8-10th fellows of the periodic table.
[Claim 5]A manufacturing method of the carbon nano fiber according to any one of claims 1 to 4 contacting material gas for a catalyst at 550-800 **.
[Claim 6]A manufacturing method of the carbon nano fiber according to any one of claims 1 to 5 when a carbon nano fiber to generate observes with a scanning electron microscope, wherein a path of a direction right-angled to a fiber axis is 10-800 nm.
[Claim 7]A manufacturing method of the carbon nano fiber according to any one of claims 1 to 6, wherein a carbon nano fiber to generate contains what has the platelet structure of having right-angled graphene to a fiber axis.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the manufacturing method of the carbon fiber which has a carbon nano fiber, i.e., the super-thin fiber diameter of a NANOMETORU (nm) order. This invention relates to the method of manufacturing a carbon nano fiber using the cheap catalyst which may be obtained easily, in detail.
[0002]
[Description of the Prior Art]The thing which is called a carbon nano fiber by kind of carbon fiber and to which a fiber diameter changes from black lead-like carbon at about 10-500 nm is known. It is thought that this thing is promising as a hydrogen absorption material or an electrode active material of a lithium ion battery. The method of contacting the material gas which contains carbon compounds in this under an elevated temperature by making metal particles, such as nickel, iron, and cobalt, into a catalyst as a manufacturing method of a carbon nano fiber, and making a carbon deposition reaction occur on a catalyst is known. by this method, it was thought that the fiber diameter of the carbon nano fiber to generate was in agreement with the primary particle diameter of the catalyst to be used -- a sake -- a catalyst -- the very small thing of particle diameter should be used as metal particles -- it thought. For example, the thing which obtained it at 200-600 ** in it by carrying out the pyrolysis of the organic metallic compound to the patent No. 3117523 gazette and for which 50 nm or less of carbon nano fibers are preferably manufactured by making about 10-nm metal particles into a catalyst is indicated. However, this method is difficult to prepare homogeneous high metal particles, and by-products, such as soot, generate it besides a carbon nano fiber. In JP,2001-98429,A, carriers, such as silica, alumina, and magnesia, are impregnated with metal salt, and the dry thing for which carry out after hydrogen reduction, metal particles of 50 nm or less are made to generate, and a carbon nano fiber is manufactured by making this into a catalyst is indicated.
[0003]
[Problem(s) to be Solved by the Invention]One of the problems of the manufacturing method of the conventional carbon nano fiber is that preparation of an ultrafine particle-like metal catalyst is difficult. Separation with the carbon nano fiber and catalyst which were generated is also difficult. Therefore, this invention tends to provide the method of manufacturing a carbon nano fiber by a easier method.
[0004]
[Means for Solving the Problem]According to this invention, a carbon nano fiber can be industrially manufactured advantageously by contacting material gas containing carbon compounds for a catalyst to which an overall diameter changes from metal of 1 micrometers or more substantially, and making a carbon deposition reaction occur for it.
[0005]
[Embodiment of the Invention]In this invention, the overall diameter of a primary particle uses as a catalyst what comprises metal of 1 micrometers or more substantially. Although it was thought that a catalyst needed to be an ultrafine particle of particle diameter comparable as the fiber diameter of the carbon nano fiber to generate conventionally, This invention persons found out

the metal particles of a large diameter, and that a carbon nano fiber generated efficiently even if it uses metal, such as tabular [except granular], mass, a line, and porous state, as a catalyst further farther than the fiber diameter of a carbon nano fiber. Thus, although a carbon nano fiber can be made to generate regardless of the shape of a catalyst, it is preferred to usually use a granular catalyst. As for especially the overall diameter, it is usually preferred that it is 1 mm or less 10 mm or less, considering preparation of a catalyst, and the production efficiency of a carbon nano fiber. Usually, it is preferred that an overall diameter uses the catalyst which comprises substantially especially the metal particles which are 5-300 micrometers 1-500 micrometers. Considering an ease, catalyst efficiency, etc. of catalyst preparation, it is preferred that the thing of the range whose overall diameter is about 50-200 micrometers, i.e., 280-70 meshes, uses what occupies especially not less than 70% not less than 50%. As metal of a catalyst, these alloys [of the periodic table] of five to 11 fellows, such as metal, for example, nickel, cobalt, molybdenum, iron, copper, vanadium, and palladium, are used. It is preferred to use iron, nickel, cobalt or these alloys especially iron, or an iron alloy especially.

[0006]Preparation of a catalyst can be easily performed by the method of returning an oxide, hydroxide, etc. of the method of grinding metal or an alloy mass, or desired particle diameter. If it is a request, a catalyst can also be prepared by the pyrolysis of an organic metallic compound, etc. A carbon nano fiber is manufactured by accommodating this catalyst in a reactor, supplying the material gas which contains the carbon compounds of a raw material in this at an elevated temperature, and making a carbon deposition reaction occur. What is necessary is just to use hydrocarbon, such as carbon monoxide, carbon dioxide, methane, ethane, acetylene, benzene, toluene, as carbon compounds of a raw material. It is preferred to use carbon monoxide especially. It is preferred to make hydrogen contain in material gas. Generally coexistence of hydrogen gives the carbon nano fiber of a high grade. As for hydrogen, it is preferred to make it 0.1-10 mol-double-exist to the carbon compounds of a raw material. Inactive gas, such as the compound of further others, for example, nitrogen, and argon, may be made to contain in material gas. However, since coexistence of gas besides these makes the gas volume supplied to a reactor increase, coexistence of a lot of gas of other should be avoided.

[0007]Although a reaction is usually performed at 400-1200 **, it is preferred to carry out at 550-800 ** especially 400-1000 **. A reaction supplies the gas which contains the carbon compounds of a raw material in the reactor which accommodated the catalyst, The gas and the catalyst which contain coal-for-coke-making-ized hydrogen in reactors, such as a batch method which makes the generated carbon nano fiber deposit on a catalyst, and a rotary kiln, can be supplied continuously, and which method of the continuous method continuously discharged from a reactor can also perform the generated carbon nano fiber and a catalyst. Usually, although it is made to react by a batch method, it is preferred to supply especially the gas which contains the carbon compounds of a raw material per 1g of catalysts in this case at the rate of flow for 10 - 10^3ml/by 1 - 10^4ml/under ordinary pressure.

[0008]When manufacturing a carbon nano fiber, soot and others carry out a byproduction simultaneously. Although graphite structure is [carbon nano fiber] developed, graphite structure is [by-products, such as soot,] seldom developed. Therefore, the powder X diffraction of a resultant can be measured, and it can have a degree of graphitization computed by the formula (new carbon industry 65 pages, a modern edit company, Showa 55) of the following mailing from the value of average interlayer spacing d_{002} of a graphite side, and can be considered as the index of the purity of a carbon nano fiber.

[0009]Generally the carbon nano fiber obtained by [the interlaminar distance (A) of 3.44-graphite] / dawn method from degree-of-graphitization (%) =[0.086] x100 has a high degree of graphitization, and, in many cases, the degree of graphitization has usually reached to not less than 90% not less than 80%. Although it is known that three kinds, a vertical platelet structure, parallel ribbon structure, and the herringbone structure of V character, exist in a carbon nano fiber to a fiber axis in a graphite side, According to the transmission electron microscope photograph, what is obtained by this invention method has platelet structure.

[0010]

[Example]An example explains this invention still more concretely below.
The thing with a particle diameter of 90–250 micrometers was acquired from the reduced iron powder (made by Kishida Chemical Co., Ltd.) of example 1 marketing by screen analysis. The coil made from quartz 40 mm in diameter and 480 mm in length was made to distribute 0.3 g of this iron powder, and it accommodated. Supplying the mixed gas of the mole ratio 1:1 of carbon monoxide and hydrogen by a part for 68–ml/at a room temperature under ordinary pressure, temperature up of the coil was carried out to the coil to 650 **, and it was made to react to it for 129 minutes at this temperature. The coil was cooled radiationally and the carbon nano fibers 0.839g were collected. The degree of graphitization of this thing was 94%. The scanning electron microscope photograph of this carbon nano fiber is shown in drawing 1, and a transmission electron microscope photograph is shown in drawing 2. Drawing 1 shows that the fiber diameter of this carbon nano fiber is about 200 nm. It turns out that it is the platelet structure of having a vertical graphene structure from drawing 2 to a fiber axis.
[0011]The carbon nano fiber was manufactured like Example 1 except having used the pure iron powder (product made from High grade Chemicals) of two to example 5 marketing as a catalyst. A result is shown in Table 1. In about 200 nm, the fiber diameter of each obtained carbon nano fiber was a thing of platelet structure.
[0012]
[Table 1]

表1

	触媒の粒径 (μm)	カーボンナノファイバー生成量 (mg)	黒鉛化度 (%)
実施例2	150	1085	96
実施例3	53	1170	99
実施例4	5	1200	83
実施例5	2～3	926	96

The carbon nano fiber was manufactured like Example 1 except having used as a catalyst what immersed the example 630mmx100mmx1mm griddle in the 1–N chloride of the room temperature for 1 hour, and washed the surface. The carbon nano fibers 0.86g deposited on the griddle were collected. The fiber diameter of this thing was about 200 nm.
[0013]The coil made from quartz 40 comparative example 1 mm in diameter and 480 mm in length was heated at 850 **. The mixed gas (mole ratio 1:1) of the carbon monoxide and hydrogen containing $Fe(CO)_5$ was supplied to this by a part (ordinary pressure, room temperature) for 68–ml/, and the carbon nano fiber was made to generate. It performed making $Fe(CO)_5$ contain in mixed gas by passing the inside of the $Fe(CO)_5$ liquid which held mixed gas at 0 **. The reaction was performed for 129 minutes and 500 mg of carbon nano fibers were obtained. The degree of graphitization of this thing was 72%.
[0014]Except having heated comparative example 2 coil at 550 **, it was made to react like the comparative example 1, and 70 mg of output was acquired. The degree of graphitization of this thing was 27%.
Except having used for comparative example 3 magnesia 0.2 g of 5%Fe/MgO catalysts which supported iron, it was made to react like Example 1 and the output 0.233g was acquired. The degree of graphitization of this thing was 34%. As a result of measuring an iron grain child's overall diameter in the above comparative examples 1–3 with light scattering measurement, a transmission electron microscope, a scanning electron microscope, etc., all were 200–300A.

[Translation done.]